# SCIENCE FOR GLASS PRODUCTION

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## STRUCTURE AND PROPERTIES OF ERBIUM–TITANIUM–TELLURITE GLASS

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The structure of glasses of the compositions $x\mathrm{Er_2O_3} - 2x\mathrm{TiO_2} - (100 - 3x)\mathrm{TeO_2}$ was investigated and the glass formation region, situated in the range of $2 < x < 7$ was established. The possibility of increasing the glass transition temperature and consequently the thermal stability of erbium tellurite glass by doping with titanium (IV) oxide was demonstrated.

The number of publications on development and investigation of active media based on tellurite glasses has increased significantly in recent years. This is because $TeO_2$ glass has high refractive indexes ($n > 2.0$), high transparency, including in the near IR region of the spectrum (0.35 – 6.00 μm) [1], the possibility of varying the compositions of the glass within wide limits, and higher solubility of the cations of rare-earth elements in comparison to quartz glass. The last two circumstances allow obtaining a much broader luminescence band of $Er^{3+}$ (about 80 nm) in fibers made of tellurite glass than with quartz fibers (about 35 nm) [1, 2], which is necessary for simultaneously enhancing some signals in current WDM (wavelength-division multiplexing) networks. For this reason, broad-band fiber amplifiers based on tellurite glass with $Er^{3+}$ dopants are now being actively developed [1 – 3]. The main drawback of tellurite glass, which is related to the low glass transition temperature (about 290°C) and prevents it from being used in conditions of intensive radiation, can be partially eliminated by complicating the composition of the glass and doping with high-melting oxides, for example, $WO_3$, $Nb_2O_5$, etc. [1 – 3].

For this reason, the system $Er_2O_3 - TiO_2 - TeO_2$ (ETT) is of special interest. The high-melting oxides ($Er_2O_3$ and $TiO_2$) in it makes the possibility of developing new laser glasses that have high thermal stability and chemical resistance in comparison to the investigated analogs of laser tellurite glasses very attractive. In addition, the possibility of separating active $Er_2Ti_2O_7$ crystals with the structure of pyrochlore and the fluorite-like phase $Er_2Te_5O_{13}$, which has been studied very little, in the glasses of this system offers new prospects for developing glass ceramic materials with a high $Er^{3+}$ content ($> 5 \times 10^{20}$ cm$^{-3}$) and improved luminescence characteristics. Such materials are of great interest as the active elements of tunable and fiber lasers, laser microchips, and broadband signal amplifiers.

However, almost nothing is known of glass formation in the ETT system. There is thus no information on the structure and crystallization of erbium–titanium–tellurite glasses and its effect on the luminescence-spectral properties.

We synthesized and investigated glasses in which $Er_2O_3 : TiO_2 = 2$, and the composition can be expressed by the general formula $x\mathrm{Er_2O_3} - 2x\mathrm{TiO_2} - (100 - 3x)\mathrm{TeO_2}$. This ratio was selected for the purpose of subsequently fabricating glass ceramic materials containing $Er_2Ti_2O_7$ with the same $Er_2O_3 : TiO_2$ ratio from these glasses.

We found that transparent glasses in the $x\mathrm{Er_2O_3} - 2x\mathrm{TiO_2} - (100 - 3x)\mathrm{TeO_2}$ system can be fabricated in the range of $2 < x < 7$. The glasses were melted in corundum crucibles at 850°C for 30 min. The glass melt was then poured onto a metal plate and sheets 1 – 2 mm thick were obtained by compression molding. The DTA curves of monolithic samples of the glasses (Fig. 1) were recorded at the rate of 10°C/min with a Netzsch DSC 404 high-temperature thermal analyzer using $Al_2O_3$ powder as the standard. The characteristic glass transition temperature $t_g$, crystallization tem-

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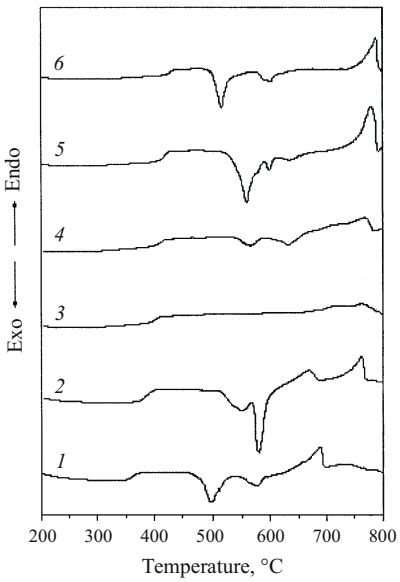


**Fig. 1.** DTA curves of erbium–titanium–tellurite glasses: *1*, *2*, *3*, *4*, *5*, and *6* ) $x$ = 2, 3, 4, 5, 6, and 7, respectively.

perature $t_{x\text{I}x\text{II(exo)}}$, and melting point $t_{m\text{(endo)}}$ determined with the DTA curves are reported in Table 1.

It follows from the DTA curves and data in Table 1 that the glasses of the ETT system are characterized by higher glass transition temperatures than other laser glasses based on $TeO_2$ [1 – 3]. This is responsible for the higher thermal stability of these glasses, one of the most important characteristics in using a material in conditions of intensive laser radiation. It should be noted that the increase in the glass transition temperature in these glasses is not only caused by an increase in the $Er_2O_3$ and $TiO_2$ in them, but also to the inevitable presence of $Al_2O_3$ in the glasses due to dissolution of the corundum crucibles. As indicated in [4, 5], aluminum oxide is a constituent part of most laser glasses, since aluminum inhibits clustering of rare-earth element cations and causes their uniform distribution within the glass lattice. For this reason, the presence of $Al_2O_3$ in the investigated glasses should be considered as an auxiliary dopant that improves the physicochemical and luminescence properties.

Almost all of the glasses investigated tend to crystallize. In particular, the presence of two exothermic peaks on the DTA curves, probably caused by crystallization of no less

**TABLE 1**

| Molar content $x$, % | $t_g$, °C | $t_{x\text{I(exo)}}$, °C | $t_{x\text{II(exo)}}$, °C | $t_{m\text{(endo)}}$, °C |
|---|---|---|---|---|
| 2 | 360 | 500 | 578 | 690 |
| 3 | 382 | 546 | 580 | 763 |
| 4 | 399 | – | – | – |
| 5 | 410 | 560 | 635 | 772 |
| 6 | 423 | – | 638 | 785 |
| 7 | 430 | – | 600 | 790 |

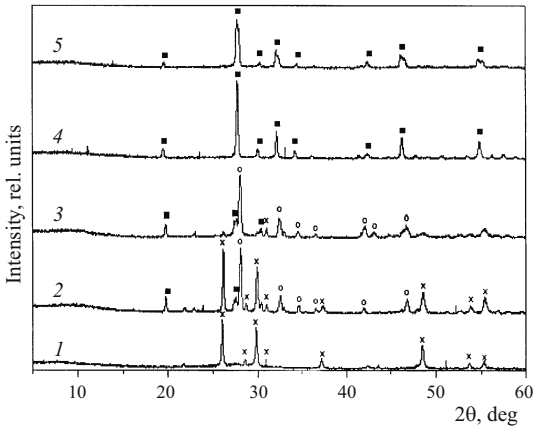


**Fig. 2.** Diffractograms of crystallized erbium–titanium–tellurite glasses: *1*, *2*, *3*, *4*, *5* ) $x$ = 2, 3, 5, 6, and 7, respectively; ×) $TeO_2$; ○) $TiTe_3O_8$; ■) $Er_2Te_5O_{13}$.

than two different phases, is characteristic of compositions with a molar content of less than 4% $Er_2O_3$. On the contrary, glass of the composition $4Er_2O_3 \cdot 8TiO_2 \cdot 88TeO_2$ is characterized by the absence of peaks on the DTA curve, which indicates its high resistance to crystallization and allows considering this glass composition as a promising base for designing thermostable and chemically resistant tellurite glasses for fiber amplifiers.

The crystalline phases distinguished in glasses of the compositions $x\text{Er}_2\text{O}_3 - 2x\text{TiO}_2 - (100 - 3x)\text{TeO}_2$ were identified by XPA (Fig. 2). The data obtained are in complete agreement with the results in [6], where the structure and properties of binary glasses of the systems $Ln_2O_3 - TeO_2$ and $XO_2 - TeO_2$ (X = Zr, Sn, Hf) were investigated. As Fig. 2, curve *1*, shows, crystallization of glass of the composition $2Er_2O_3 \cdot 4TiO_2 \cdot 94TeO_2$ is accompanied by separation of only one crystalline phase — tetragonal $TeO_2$. A further increase in the content of $Er_2O_3$ and $TiO_2$ in the glass significantly alters the character of crystallization and leads to separation of several phases.

Crystallization of glass of the composition $3Er_2O_3 \cdot 6TiO_2 \cdot 91TeO_2$ (see Fig. 2, curve *2* ) is accompanied by separation of two phases — tetragonal $TeO_2$ and $TiTe_3O_8$ with a cubic body-centered lattice. A similar phase composition was observed in [6] in crystallization of glass of the composition $5XO_2 \cdot 95TeO_2$ (X = Zr, Sn, Hf). This forms the basis for hypothesizing that a molar content of less than 5% $Er_2O_3$ does not affect the character of crystallization of erbium–titanium–tellurite glasses.

However, with a further increase in the $Er_2O_3$ content, gradual degeneration of $TeO_2$ and $TiTe_3O_8$ phases is observed (see Fig. 2, curve *3* ), and crystallization causes separation of a single product of the composition $Er_2Te_5O_{13}$ with a cubic face-centered lattice and a fluorite-like structure [7, 8], as indicated by the x-ray patterns of crystallized glasses of the compositions $6Er_2O_3 \cdot 12TiO_2 \cdot 82TeO_2$ (see

Fig. 2, curve *4*) and $7Er_2O_3 \cdot 14TiO_2 \cdot 79TeO_2$ (see Fig. 2, curve *5*). These results are in agreement with the data in [8], which reports separation of $Er_2Te_5O_{13}$ crystalline phase from high-erbium glasses of the $Er_2O_3 - BaO - TeO_2$ system and its effect on the hardness of the glass ceramic obtained. It should be noted that the low glass-forming power of the $7Er_2O_3 \cdot 14TiO_2 \cdot 79TeO_2$ composition did not allow obtaining transparent samples of these glasses and considering them as objects for further investigation. For this reason, the $6Er_2O_3 \cdot 12TiO_2 \cdot 82TeO_2$ composition is the most promising composition for creating transparent glass ceramics with a high erbium content.

The observed character of crystallization of these ETT system glasses is caused by changes in their structure. The Raman spectra (RS) of glasses of the $xEr_2O_3 - 2xTiO_2 - (100 - 3x)TeO_2$ system, characterized by the set of bands around 450, 660, and 780 $cm^{-1}$ characteristic of tellurite glasses, are shown in Fig. 3. The tellurium atom in $TeO_2$ is in the vicinity of six oxygen atoms, and the Te – O distances are 2.05, 2.07, 2.12, 2.20, 2.68, and 2.79 Å [9]. Acceding to the data from this study, there is also significant anisotropy of the tellurium oxide polyhedrons in tellurite glasses, in which the Te – O distances vary from 2.05 to 2.80 Å. Since four of the oxygen atoms are much closer to the tellurium atom than the other two, the coordination number of tellurium with respect to the chemical bond is equal to 4, although crystallographically it is equal to 6.

For this reason, it is assumed that all tellurite glasses are based on trigonal bipyramids of $TeO_4$ joined primarily at the apices with formation of a continuous three-dimensional skeleton. The band in the 450 $cm^{-1}$ region characteristic of tellurite glasses carries information on the stretching vibrations of apical Te – O – Te bonds that join the trigonal $TeO_4$ bipyramids. The bands in the region of 660 $cm^{-1}$ describe the stretching vibrations of asymmetric Te – O – Te bonds, while the band around 780 $cm^{-1}$ corresponds to stretching vibrations of the Te = O, $Te - O^-$ bonds in $TeO_{3+1}$ or $TeO_3$ polyhedrons and thus bears information on the degree of coherence of the skeleton. The RS of glass of the composition $2Er_2O_3 \cdot 4TiO_2 \cdot 94TeO_2$ (see Fig. 3, curve *1*) is characterized by intensive bands in the 450 and 660 $cm^{-1}$ regions, which allows judging the high degree of coherence of the skeleton not only at the apices but also along the edges of $TeO_4$ polyhedrons, caused by the relatively low content of $Er_2O_3$ and $TiO_2$ modifiers. To a great degree, this determines the character of crystallization and explains separation of tetragonal $TeO_2$ in this stage.

As the modifier content increases, apical Te – O – Te bonds break, which is accompanied by an increase in the number of nonbridge oxygen atoms and transformation of trigonal $TeO_4$ bipyramids into $TeO_{3+1}$ $TeO_3$ polyhedrons. In the RS, the decrease in the intensity of the bands around 450 and 660 $cm^{-1}$ and the increase in the intensity of the band at 780 $cm^{-1}$ correspond to these changes. An increase in the number of nonbridge oxygen atoms increases the portion of

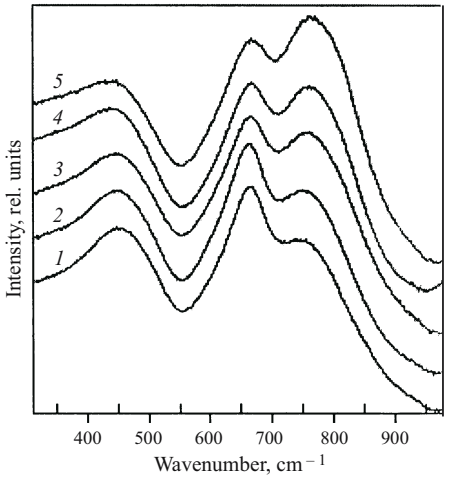


**Fig. 3.** Raman spectra of erbium–titanium–tellurite glasses: *1*, *2*, *3*, *4*, and *5*) $x$ = 2, 3, 4, 5, and 6, respectively.

trigonal $TeO_4$ bipyramids with common edges both with each other and with $TiO_6$ octahedrons. This increases the rigidity of the structural skeleton and separation of several crystalline phases, which was observed in crystallization of $3Er_2O_3 \cdot 6TiO_2 \cdot 91TeO_2$ and $5Er_2O_3 \cdot 10TiO_2 \cdot 85TeO_2$ compositions (see Fig. 3, curves *2* and *3*).

We can hypothesize that glass of the composition $6Er_2O_3 \cdot 12TiO_2 \cdot 82TeO_2$ is characterized by the highest number of nonbridge oxygen atoms, as the highest intensity of the band around 780 $cm^{-1}$ in the RS indicates (see Fig. 3, curve *5*). This finding, together with the XPA data (see Fig. 2, curve *4*), suggests that a further increase in the $Er_2O_3$ content in tellurite glasses not only causes a decrease in the proportion of structural titanium and tellurium tetrahedrons with common sides but also segregation of $Er^{3+}$ due to the low solubility of rare-earth element cations in glasses [5]. The last circumstance determines the further character of crystallization and separation of $Er_2Te_5O_{13}$ phase.

Since our studies of crystallization of glasses of $xEr_2O_3 - 2xTiO_2 - (100 - 3x)TeO_2$ compositions demonstrated the impossibility of separation of an $Er_2Ti_2O_7$ phase with the structure of pyrochlore, we can hardly expect any important improvement in the luminescence properties of heat-treated samples of glasses of the composition $6Er_2O_3 \cdot 12TiO_2 \cdot 82TeO_2$. However, separation of the barely studied crystalline $Er_2Te_5O_{13}$ phase will allow fulfilling the possibility of developing high-erbium nanostructured titanium–tellurite glasses containing mixed crystals (solid solutions) of $Er_xA_{1-x}Te_5O_{13}$ ($A = Ln^{3+}$, $Y^{3+}$, $Cr^{3+}$).

The possibility of regulating the Er – Er distance by varying the Er : Ln ratio and consequently controlling the luminescence-spectral properties of the material was proposed in [10] on the example of solid solutions of the composition $Er_xLn_{1-x}Ti_2O_7$. This approach can also be implemented in the case of the $Er_2Te_5O_{13}$ crystalline phase. The composition of the glass studied here $6Er_2O_3 \cdot 12TiO_2 \cdot 82TeO_2$, in which

some of the erbium ions will be substituted by $Ln^{3+}$, $Y^{3+}$, or $Cr^{3+}$, could be used as the basis. By controlling the ratio of erbium and the coactivator, it is possible to regulate the composition of the $Er_xA_{1-x}Te_5O_{13}$ crystalline phase, and also controlling the luminescence-spectra properties of the material.

Another approach consists of solid-phase synthesis of $Er_xA_{1-x}Te_5O_{13}$ crystals and incorporating them in low-melting glass based on $TeO_2$ with the technology proposed in [11 – 13]. By controlled dissolution of these crystals in the matrix of the glass, transparent glass composites with a micro- or nanocrystalline structure can be obtained. This approach is more general than traditional synthesis of transparent glass-ceramic materials by nanostructuring in the initial stage of phase separation. However, due to insufficient investigation of the composition approach, a detailed study of the possibilities of this method is necessary.

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